

### Abstract

The present invention is a process for the preparation of  $17\beta$ -hydroxy- $7\alpha$ -methyl-19-nor- $17\alpha$ -pregn-5(10)-en-20-yn-3-one ( $17\alpha$ -ethynyl- $17\beta$ -hydroxy- $7\alpha$ -methyl-5(10)-estren-3-one, tibolone) of formula 1, which comprises hydrolysis of  $17\alpha$ -ethynyl- $17\beta$ -hydroxy- $7\alpha$ -methyl-5(10)-estrene 3,3-cyclic ketals of formula 2, where groups  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are hydrogen atoms or alkyl groups, or  $R_1$  and  $R_3$ , taken together with the carbon atoms within the dioxolane ring to which they are attached, form an alicyclic ring fused to the dioxolane ring, with  $R_2$  and  $R_4$  being hydrogen atoms, or  $R_1$  and  $R_3$  together with the carbon atoms to which they are attached form an aromatic ring fused to the dioxolane ring, where  $R_2$  and  $R_4$ , taken together, form a chemical bond within said aromatic ring. In addition, the present invention includes an intermediate, compound of formula 2 and two processes to prepare  $17\alpha$ -ethynyl- $17\beta$ -hydroxy- $7\alpha$ -methyl-5(10)-estrene 3,3-cyclic ketals of formula 2: (a) by contacting  $17\alpha$ -ethynyl- $17\beta$ -hydroxy- $7\alpha$ -methyl-4-estren-3-one with vicinal diols in the presence of a protic acid, and (b) by contacting  $7\alpha$ -methyl-5(10)-estrene-17-one 3,3-cyclic ketals of formula 4, where  $R_1-R_4$  are defined as above, with metal acetylides, in inert solvents.